

THE NATURAL AND PERTURBED TROPOSPHERE

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SUMMARY

The troposphere is a region of great chemical complexity, and many human activities may alter the chemical structure of the region. Any realistic assessment of human impacts on pollution and climate requires an understanding of the natural budgets of atmospheric gases. This understanding, in turn, requires a detailed knowledge of physical, chemical, and biological processes within the various reservoirs which are involved in the cycles of these gases. This paper first reviews the processes important in establishing the concentrations of a number of tropospheric species and discusses gaps in current understanding of these processes. The points at which man may intervene in the major cycles of atmospheric gases are identified and the possible consequences of such interventions are described. Pollutants released into the troposphere may adversely affect the environment by virtue of their chemical interactions with other atmospheric species, their radiative properties, or both. Problems discussed in this review include the growth of atmospheric carbon dioxide (CO_2) resulting from the burning of fossil fuels and its possible climatic effects, the consequences of increased levels of carbon monoxide (CO) emission on the self-cleansing ability of the troposphere and on the radiation budget, and possible changes in the stratospheric odd nitrogen and ozone amounts due to increased use of fertilizers in agriculture. The magnitude of the perturbations predicted by various model studies are reviewed with particular attention to uncertainties which may affect the results.

INTRODUCTION

Although problems of urban pollution have been studied for many years, the fact that the global-scale troposphere is an extremely complex chemical system subject to a variety of anthropogenic perturbations is only now being appreciated. Various aspects of the photochemistry of the natural troposphere have been described by several authors (refs. 1 to 3). An understanding of the chemical, biological, and physical processes affecting the concentrations of trace species in clean tropospheric air is clearly a prerequisite to any realistic assessment of the effects of human activities on the state of the atmosphere. Although major problems remain in identifying sources, sinks, and chemical reaction paths for some species, it does appear that tropospheric models can be constructed which are consistent with much of the present knowl-

edge of the concentrations of trace species and their chemical reaction rates. At least a qualitative understanding of the impact of industrial activities on the global-scale troposphere may be attempted.

Changes in the natural abundance of trace species are of concern for one or both of two reasons. A particular gas may absorb infrared (IR) radiation emitted by the Earth's surface and contribute to the greenhouse effect and the climatic state. Changes in the concentration of such a gas would thus have a direct influence on climate. The spectral region from about 8 to 12 μm is of particular importance since it includes the central portion of the Planck spectrum radiated by the Earth and is also a relatively clear "window" in which few natural constituents absorb strongly. Other species have undesirable chemical properties; for example, they may be toxic substances. Still other gases may possess both thermal and toxic properties. It is also possible that a species which is innocuous in itself may, through chemical interactions, alter the concentrations of harmful species. The problems involved in studying the impact of anthropogenic emissions can be quite complex and have many ramifications.

The study of the chemical and climatic effects of industrial emissions into the atmosphere is just beginning, and a quantitative assessment of these effects requires an understanding of the complex interactions of species within the atmosphere and of the atmosphere with other physical systems such as the oceans, lithosphere, and biosphere. In this paper, current knowledge of the budgets of various species in the natural troposphere is reviewed, and man's intervention in these budgets and possible consequences of such intervention are discussed.

ABUNDANCES OF TROPOSPHERIC GASES

The concentration of a particular species is determined by competition between various production and loss processes. These processes may consist of physical, biological, or chemical interactions between the atmosphere and other geological systems or they may consist of chemical and physical interactions within the atmosphere itself. With the exception of the noble gases, all elements in the atmosphere undergo exchange processes between the atmosphere and other reservoirs. The sum of these exchange processes constitutes a cycle for the element (or species) in question, and the average time an atom or molecule spends in a particular reservoir is its lifetime or residence time in that reservoir.

A convenient way of considering the multitude of trace species of importance in the troposphere is to organize them into certain elemental groups as shown in table I. The first two columns of this table give the name and chemical symbol of various tropospheric species. The third column gives the mixing ratio, which for most species must be calculated since their abundances are too small to measure. Those species concentrations which have been measured are indicated by a footnote; calculated values were derived by the present authors and represent daytime-averaged mid-latitude values. The lifetime of a species (fourth column) is related to its mixing ratio in that those which are highly reactive and have short lifetimes will generally not be abundant. Absorption bands in the thermal IR region are indicated in the fifth column. The sixth and seventh columns of table I indicate whether the sources and sinks for a

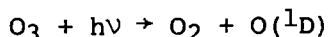
particular species are primarily anthropogenic (A), biological or microbiological (B), chemical reactions in the atmosphere (C), or physical (P). Some of the information in the table was taken from references 4 to 20; these sources are given in the eighth column.

OXYGEN GROUP

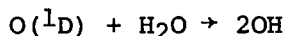
The most abundant member of this group, molecular oxygen (O_2), is a major constituent comprising about 20 percent of the atmosphere. The oxygen cycle has been reviewed by Walker (ref. 21) and by several others (refs. 22 to 24) in the context of discussions of the carbon cycle. To address the question of intervention by human activities in the oxygen cycle, it must be noted that there are two different time scales in which oxygen is exchanged between the atmosphere and terrestrial reservoirs. The shorter of these time scales involves the exchange of about 3×10^5 million metric tons per year (3×10^5 Mt/yr) of oxygen between the atmosphere and biosphere via processes of photosynthesis and respiration and decay. The reservoir of atmospheric oxygen involved in this exchange ($\sim 10^9$ Mt) is much larger than the reservoir of biospheric carbon ($\sim 3.5 \times 10^6$ Mt) or of available fossil fuels ($\sim 7 \times 10^6$ Mt). Since 2.67 Mt of O_2 will oxidize 1 Mt of carbon, human intervention in the carbon cycle, either through nearly complete combustion of available fossil fuels or through substantial alterations in the populations of photosynthesizing organisms, will have small (less than 4 percent) impact on the atmospheric O_2 abundance over times of the order of hundreds of years.

The longer time scale involves the exchange of O_2 between the atmosphere and crustal sediments. The source of oxygen on this scale is due to about 300 Mt/yr of O_2 produced by photosynthesis which is not utilized in the oxidation of dead organic carbon. The stoichiometric equivalent amount of carbon is sequestered in ocean sediments. A corresponding sink of 300 Mt/yr for O_2 results from erosion and weathering of these sediments as they are again exposed to the atmosphere. The reservoir of sedimentary carbon contains about 5.5×10^{10} Mt and could readily absorb all the O_2 presently in the atmosphere if the O_2 source were extinguished. The time over which this would occur is about 10^9 Mt/(300 Mt/yr) or ~ 3 million years. Because of the long time scale involved in potential human impacts on the oxygen cycle, it will not be discussed in detail; instead, some problems of more immediate concern involving other members of the oxygen group are discussed in the following paragraphs.

Ozone (O_3) is the next most abundant member of the oxygen group and is a chemically important tropospheric constituent. Almost all tropospheric photochemistry is initiated by the photolysis of ozone in the 300 to 310 nm region of the ultraviolet (UV) spectrum. The reaction is

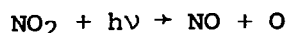


The $O(^1D)$ thus formed may then react with water vapor



to give two, highly reactive hydroxyl radicals (OH) which initiate several com-

plex reaction chains. Another potential precursor of tropospheric photochemistry is nitrogen dioxide (NO_2) which can dissociate over the UV wavelength range from 300 to 400 nm:

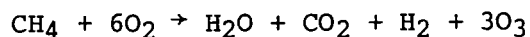


Both O and NO are involved in subsequent chemical reactions.

The oxygen budget of the troposphere is represented schematically in figure 1. This figure indicates that NO_2 photolysis and downward transport from the stratosphere are primary sources of tropospheric ozone. Photolysis of this ozone results in $\text{O}(^1\text{D})$ and, after reaction of $\text{O}(^1\text{D})$ with H_2O , in OH radicals. These in turn oxidize methane and other hydrocarbons to produce more ozone. Ozone is lost via reactions with NO_x (NO and NO_2) and HO_x (OH and HO_2) radicals. The lesser sink due to reaction at the ground is not indicated in figure 1.

A problem that has generated much recent debate is that of the sources and sinks of tropospheric ozone. The "classical" view has been that ozone, created as a result of O_2 dissociation by UV radiation with wavelengths less than 240 nm, is transported downward and destroyed at the ground (ref. 25). The observed ground-level background ozone concentration is about 3 ppbm (parts per hundred million), and if downward transport and ground-level destruction are in fact the major source and sink mechanisms for tropospheric ozone, its lifetime is of the order of 1 month. Chameides and Walker (refs. 26 and 27) proposed an alternative view, that ozone in the lower troposphere is photochemically created, especially as a consequence of the methane oxidation chain. The role of reactive hydrocarbons in ozone production in polluted urban air is well known (refs. 3 and 28), and the possible importance of the much less reactive but more abundant methane in the global-scale production of ozone was noted by Crutzen (ref. 29).

The reaction scheme by which methane (CH_4) oxidation results in ozone production is discussed by Fishman and Crutzen (ref. 30). The net effect, which is the sum of 15 individual reactions, is



This reaction sequence essentially extracts O_2 molecules from the ambient reservoir and makes their component atoms available for ozone formation. It thus provides an alternative to the direct splitting of O_2 by UV radiation, which does not occur in the troposphere.

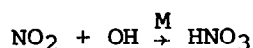
The importance of transport in establishing the tropospheric ozone abundance is supported by observational evidence on the latitudinal distributions of this constituent. The tropospheric ozone burden (total amount of ozone in a column) shows maxima in regions of enhanced troposphere-stratosphere exchange, 30° , 45° , and 60° latitude (refs. 5 and 31). Photochemical models have not addressed the problem of the observed latitudinal distribution of ozone, but there is no obvious photochemical argument which might account for it.

The sharp disagreement between the conclusions of the photochemical models of Chameides and Walker (refs. 26 and 27) and the arguments supporting a purely

dynamic source for tropospheric ozone has motivated additional model studies (refs. 32 and 33). The results of these more recent calculations indicate that photochemical production alone cannot account for observed levels of tropospheric ozone and that, in fact, the troposphere acts as a net chemical sink. In the calculation of Chameides and Stedman (ref. 32), 70 percent of the ozone in a typical mid-latitude tropospheric column is produced by downward transport from the stratosphere and 30 percent is photochemically produced. In this typical column, 70 percent of the ozone is chemically destroyed and 30 percent destroyed by reaction at the ground. Calculations made with the box model of Stewart et al. (ref. 33) lead to similar conclusions regarding the relative importance of transport and photochemistry in establishing the tropospheric ozone distribution.

The divergent conclusions of the newer and older photochemical models illuminate the principal problem in state-of-the-art models of tropospheric composition, which is their sensitivity to the data base used in the calculations. The most important component of this data base is the large number (usually ≥ 60) of chemical reactions used in the calculations. Rates for these reactions are constantly being revised as new experimental data become available. The most generally accepted chemical data base is provided by the compilation of Hampson and Garvin (ref. 34) in which these authors, and others cited in their publication, review the available experimental data and provide preferred values for a large body of chemical reaction rates. This review process is by its nature always somewhat dated, and there are usually more recent data of interest which must be considered in model calculations.

The different conclusions reached by the older (refs. 26 and 27) and newer (refs. 32 and 33) models of tropospheric ozone may be traced for the most part to the faster rates adopted for certain important reactions in which odd hydrogen and odd nitrogen radicals combine; for example,

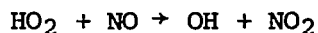


These rates were revised between publication of the older and newer models. Such reactions reduce the concentration of OH in the troposphere and thus render the methane oxidation mechanism less effective.

Another factor leading to differing conclusions in these models is the different NO₂ background adopted. The earlier models used 3 ppb NO₂, a value suggested by Robinson and Robbins (ref. 35) based on their analysis of the nitrogen budget and the sparse data then available. As additional data have become available, it has become clear that 3 ppb is too high to be representative of global background NO₂ values. The spectroscopic measurements of Noxon (ref. 11) in particular suggest that [NO₂] \lesssim 0.1 ppb. The use of lower NO₂ concentrations (\lesssim 0.5 ppb) in the more recent photochemical models reduces ozone production resulting from NO₂ photolysis.

The newer photochemical models (refs. 32 and 33) discussed previously represent a synthesis of the arguments concerning photochemical and dynamic sources for tropospheric ozone. They establish the importance of photochemical interactions in contributing to the overall ozone abundance but are consistent with the view that transport plays the major role in establishing the global

ozone distribution. Unfortunately, this consensus has proved to be short-lived. A recent measurement by Howard and Evenson (ref. 36) of the rate of the reaction,



is 8 to 20 times faster than the previously accepted values. This has extremely important consequences for the problem of production and loss of tropospheric ozone, and for tropospheric chemistry generally, since this reaction produces NO_2 , an ozone precursor, and OH, which initiates the methane oxidation chain and again produces ozone.

In the model of Stewart et al. (ref. 33) the troposphere must import 1480 Mt/yr of ozone from the stratosphere to maintain the average observed midtropospheric background value of 4.5 pphm O_3 . This transport value is consistent with that quoted in the meteorological literature (refs. 5 and 37). However, if the Howard and Evenson value for the reaction given previously is used in the Stewart et al. model, the troposphere switches from being a strong chemical sink to a strong chemical source; it must export 2000 Mt/yr of ozone. This is an unacceptable result because it is inconsistent with the observed tropospheric distribution explained previously and because the observed troposphere-stratosphere ozone gradient implies downward rather than upward transport.

Thus, the problem of the sources and sinks of tropospheric ozone remains. Even if revision of other reaction rates is found to provide a chemical sink which compensates for the chemical source given by the rate for reaction of HO_2 and NO, ozone may be found to have too short a residence time to be consistent with the indicated importance of transport in establishing its distribution.

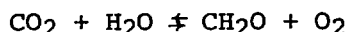
CARBON GROUP

Natural Carbon Cycle

The principal carbon-containing species in the atmosphere are carbon dioxide, methane, and carbon monoxide, which have mean concentrations of about 330 ppm, 1.4 ppm, and 0.12 ppm, respectively. Other hydrocarbons such as aldehydes, olefins, alkanes, and terpenes are generally present in much smaller amounts. Study of the global-scale effects of the carbon group on pollution and climate has centered on the three species noted. Hydrocarbons with higher molecular weights and carbon monoxide are important also in urban-scale pollution problems (refs. 28, 38, and 39). Carbon dioxide (CO_2) and methane (CH_4) are climatologically significant gases since they absorb in the thermal IR region. The contribution of CO_2 to the greenhouse effect is well known, but CH_4 has a band at 7.7 μm and changes in its abundance are also potentially important. Carbon monoxide (CO) is not active in the thermal IR region but is of concern because of its chemical properties. In high concentrations, CO is toxic; but on the global scale, concern is with its possible chemical interaction with and impact on species such as OH and CH_4 (refs. 40 and 41).

The abundance of carbon dioxide is regulated by interaction between the troposphere and biosphere (ref. 42) via the process of photosynthesis which may

be written schematically as



The forward reaction represents the utilization of CO_2 by plants in the synthesis of organic compounds represented here by formaldehyde (CH_2O). The reverse reaction represents the return of CO_2 to the atmosphere by oxidation of dead organic matter. The flow of carbon between the atmosphere and other reservoirs is shown in figure 2. Several quantitative models of the carbon cycle have been developed (refs. 22, 23, and 43 to 45) which may differ from one another and from figure 2 in the details of the adopted reservoirs and fluxes.

In figure 2, the consumption of CO_2 by the biosphere has been given as 1.5×10^5 Mt/yr, 1.1×10^5 by the land biomass and 4×10^4 by the ocean biomass. These numbers, like most of the flux and reservoir values of figure 2, are meant to be representative, but widely varying values can be found in the literature. The exchange of CO_2 between the atmosphere and biomass by photosynthesis is balanced to within 1 part in a thousand. The slight imbalance between consumption and release of CO_2 , represented by the sedimentation flux in figure 2, has resulted in the deposit over geologic time of a reservoir of fossil organic carbon of perhaps 1.2×10^7 Mt (ref. 46), of which about 7.3×10^6 Mt is available for exploitation.

Methane (CH_4) and carbon monoxide (CO) are less abundant, but important, members of the carbon group. Methane distribution is approximately uniform in the troposphere with a concentration of 1.4 ppm (ref. 6). At least 80 percent of tropospheric methane is produced by the anaerobic decomposition of organic matter in such places as swamps and paddy fields, and its sources are thus biological and microbiological. The remainder of the CH_4 comes from natural gas wells. A present estimate of the total source strength of CH_4 is about 10^3 Mt/yr (ref. 46) and is included in the soil respiration flux in figure 2. There are 4×10^3 Mt of CH_4 in the atmosphere which, combined with the source strength, implies an atmospheric residence time of 4 years. It is now generally believed that oxidation of methane via the reaction



provides the major sink. The effectiveness of this sink depends on the abundance of tropospheric OH radicals and on the rate of this reaction. The mean tropospheric abundance of OH is not well established. Measurements (refs. 14, 15, and 47) show it to be quite variable and theoretical arguments support OH concentrations ranging from 2×10^5 to 3×10^6 cm^{-3} (refs. 18 and 48). Adopting a rate of $k = 4.6 \times 10^{-15}$ cm^3/sec for the $\text{CH}_4 + \text{OH}$ reaction (ref. 34) gives a lifetime $\tau_{\text{CH}_4} = (k[\text{OH}])^{-1}$ ranging from 2.3 to 35 years. There is thus at

least a factor-of-10 uncertainty in the parameters determining the methane abundance.

Carbon monoxide distribution is approximately uniform vertically in the troposphere but shows a strong latitudinal gradient. The globally averaged concentration of CO is about 0.12 ppm, but there is a factor of 4 difference in mean concentrations between the Northern (0.20 ppm) and Southern (0.05 ppm)

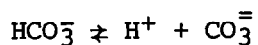
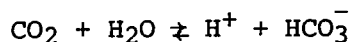
Hemispheres (ref. 8). (See fig. 3 adopted from ref. 8.) This interhemispheric concentration difference indicates the importance of Northern Hemisphere anthropogenic sources, mainly automobile and space heating, in determining the global CO abundance, but the oxidation of methane provides a strong natural source. The relative importance of these two mechanisms is still a matter of debate (refs. 49 to 51).

Perturbations to the Carbon Cycle

The long-term increase of CO₂ is the best documented of the global-scale changes in the atmospheric environment that have occurred as a result of human activities (refs. 9 and 52). Figure 4 shows monthly average values of CO₂ concentrations measured at Mauna Loa Observatory, Hawaii. The long-term increase is quite apparent. Seasonal variations in photosynthesis produce the annual cycle. Carbon dioxide absorbs in the thermal IR region, and it has been suggested by several theoretical studies that substantial increase (e.g., doubling) of CO₂ will lead to climatologically significant temperature increases in the lower atmosphere. There are two parts to a quantitative evaluation of the environmental impact of enhanced CO₂ levels: the first is to project future CO₂ concentrations as a function of time; the second is to calculate the change in surface temperature ΔT_s due to these concentrations. Each part of this problem has been addressed by several investigators, but with no consensus on either point.

The long-term increase of CO₂ has been modeled in several studies (refs. 43, 44, 53, and 54), and the results of three of these are shown in figure 5. Projections of future CO₂ levels in these model studies are obtained by solving the continuity equation for CO₂ which equates the rate of change of CO₂ in a specified reservoir to the difference between sources and sinks for that reservoir. The models shown in figure 5 use comparable source functions for the anthropogenic emission (fossil fuel burning). Hoffert (ref. 44), for example, fits a Gaussian source function to historical emission data over the 1950 to 1970 period. This source function results in consumption of about 70 percent of available fossil fuels in the 100-year period centered about the year 2069. The anthropogenic source functions used in the other two models of figure 5 differ in some details but are essentially similar in magnitude and functional form.

The two central issues in current research on this problem involve the roles of the oceans and the biomass as sources and sinks of CO₂. The substantial difference in the long-range projections of the authors cited in figure 5 is due to the differing treatments of the oceanic sink in their models. Hoffert (ref. 44) has discussed the differences between his model and that of Cramer and Myers (ref. 43) as being primarily due to treatment of the deep-ocean CO₂. In Hoffert's model, deep-ocean CO₂ is determined from the carbonic acid equilibrium,



which constrains the deep-ocean CO₂ to smaller values than in the Cramer and

Myers model in which this CO_2 is determined by exchange with the mixed layer and the ocean floor. The ability of the oceans for CO_2 uptake is smaller in Hoffert's model and thus a greater amount of CO_2 accumulates in the atmosphere. In the Keeling and Bacastow model (ref. 54), the thermal stability of the main oceanic thermocline (70 to 1000 m deep) prevents the complete mixing of CO_2 between the deep ocean and the warm surface layer, thus rendering the oceans a still less effective sink than in the Hoffert model.

Another issue which has recently been raised (refs. 55 and 56) concerns the effect of human alterations of the land biosphere, such as deforestation and agricultural expansion, on atmospheric CO_2 changes. Bolin (ref. 56) suggests that such changes in the land biota constitute a source of CO_2 equal to about 10 to 35 percent of the emission due to fossil fuel combustion. He also concludes that since this auxiliary source of CO_2 has previously gone unrecognized, the oceans must provide a more effective sink than hitherto realized. The results of Adams et al. (ref. 55) and Bolin (ref. 56) imply that the oceans are capable of absorbing 58 to 83 percent of the fossil fuel CO_2 emitted into the atmosphere. This conclusion is in sharp contrast to the trend of recent model development in which the oceans play a diminished role from that of earlier models. Broecker (ref. 57), for example, estimates that of the CO_2 emitted into the atmosphere, 52 percent remains in the atmosphere, 38 percent dissolves in the oceans, and 10 percent is assimilated by the biosphere. There is thus no current consensus as to the magnitude of the ocean sink or whether the land biota constitute a source or a sink of CO_2 .

Part of the difficulty in assessing the role of the biosphere in the carbon cycle stems from the fact that relatively small changes in the biomass would substantially alter the CO_2 flux between atmosphere and biosphere. The deforestation flux of 1000 Mt/yr shown in figure 2 corresponds to a decrease in the land biosphere of less than 0.2 percent. A similarly small increase would provide a sink of the same magnitude. As discussed subsequently in the nitrogen cycle, the ocean biomass is controlled by nutrients other than carbon.

The thermal effects of a given CO_2 increase have been studied by several authors (refs. 58 to 61), and a review of these efforts through 1975 has been published by Schneider (ref. 62). Differences in predicted surface-temperature increase ΔT_s among various one-dimensional radiative-convective models are fairly well understood in terms of differing assumptions and computational procedures. The most detailed radiative transfer calculation appears to be that of Augustsson and Ramanathan (ref. 63) who included the temperature dependence of the band absorptance in the 15- μm bands as well as the contribution to the greenhouse effect of the weak bands in the 12 to 18 μm , 9 to 10 μm , and 7 to 8 μm regions. Their result for a doubling of CO_2 concentration is a ΔT_s of 1.98 K. Manabe and Wetherald (ref. 59) have utilized a general circulation model to calculate a ΔT_s of 2.9 K (globally averaged), about 46 percent larger than the value of Augustsson and Ramanathan. In the Manabe and Wetherald model, the surface-temperature increase is greater at high latitudes because of greater thermal stability of the troposphere and decreased albedo resulting from recession of the snow boundary. This relatively large surface-temperature increase at high latitudes results in a larger globally averaged ΔT_s than is obtained with radiative-convective models.

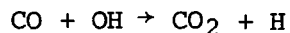
The greatest uncertainty in model calculations of surface-temperature response to increased CO₂ abundance is in the treatment of other meteorological parameters such as relative humidity and cloud amount, which may also respond to temperature changes and feedback into the CO₂ perturbation. Augustsson and Ramanathan (ref. 63), for example, show differences of up to 62 percent in ΔT_s between models with constant cloud-top altitude and others with constant cloud-top temperature.

According to Schneider (ref. 62), a present estimate of ΔT_s resulting from a doubling of atmospheric CO₂ abundance would be $1.5 \text{ K} < \Delta T_s < 3 \text{ K}$, but, as Schneider cautions, this estimate could be considerably modified by the effects of important feedback mechanisms not included in current models.

Considering the combined uncertainties of projecting future CO₂ levels and of computing ΔT_s for a given CO₂ increase, it does not seem reasonable at present to attempt a quantitative prediction of temperature increases resulting from CO₂ emissions at any specified future time. The uncertainties in the CO₂ and ΔT_s projections are indicated in figure 6 (after Baes et al. (ref. 46)). The higher of the two inner solid lines represents an assumed 4.3-percent annual growth rate in fossil fuel burning reduced in proportion to the fraction of the net supply that has been used; the lower of the two inner solid lines represents an assumed 2-percent growth rate until 2025 followed by a symmetrical decrease. The inner band in each of these cases represents the effect of a $\pm 2000 \text{ Mt/yr}$ variation in the net flux to the land, while the outer band represents the effect of varying the assumed ocean uptake from 40 to 60 percent. The right vertical axis shows the range of uncertainty in ΔT_s (as estimated by Baes et al.) for each value of CO₂ increase.

Another perturbation to the carbon group which has been discussed recently involves possible alteration of the CH₄ concentration as a result of changes in the anthropogenic CO flux into the atmosphere (refs. 40 and 41). According to calculations by Sze (ref. 40), a CO emissions increase of 4 percent per year from 1940 to 1971 followed by a 1.33 percent per year increase thereafter will result in a doubling of CH₄ concentration over its 1950 value by the year 2035. Chameides et al. (ref. 41) consider a 4.5-percent increase in CO emissions from 1976 and find an increase of CH₄ from present levels to about 2.45 ppm by the year 2010 (a 75-percent increase).

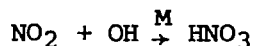
These projected CH₄ increases occur because CO is an effective scavenger of the hydroxyl radical (OH) through the reaction,



and OH is the major species capable of initiating the methane oxidation sequence. Thus, more CO results in less OH, and this in turn causes an increase in CH₄ amount.

Hameed et al. (ref. 64) have pointed out that the magnitude of the CH₄ perturbation resulting from a given CO flux increase is extremely sensitive to the NO_x background assumed in the model, and since this is presently only poorly known, quantitative statements concerning the magnitude of the CO-CH₄ perturbation are not yet feasible. According to the calculations of Hameed et al., a

doubling of the present level of CO emissions would result in an increase of CH₄ to 1.9 ppm for [NO_x] = 0.1 ppb. The reason for this sensitivity is that NO_x compounds are also effective scavengers of OH through reactions such as



The hydroxyl radical concentration is thus much more sensitive to the CO flux for low values of NO_x than for higher values.

According to Wang et al. (ref. 65), a doubling of CH₄ concentration would result in an incremental surface temperature ΔT_s of 0.28 K or 0.40 K for a fixed-cloud-top-temperature model, depending on whose absorption data are used. It is important to establish more firmly the possible magnitudes of methane increases and to study in greater detail the more general changes which would result from lowered hydroxyl radical concentrations.

NITROGEN GROUP

Natural Nitrogen Cycle

Molecular nitrogen (N₂) is the most abundant gas in the atmosphere, but it is relatively inert chemically and therefore has little direct interaction with other tropospheric species. Other forms of tropospheric nitrogen such as ammonia (NH₃), nitric oxide (NO), and nitrogen dioxide (NO₂) result from various microbiological and industrial processes which break the N₂ bond. Such processes are said to fix nitrogen in a biologically useful form. These fixation processes occur naturally in various soil and marine organisms and to a much lesser extent by the reaction of N₂ and O₂ in lightning discharges. Industrial production of fertilizer is the principal source of artificial fixation, and a debate is in progress over the degree to which this process may upset the natural cycling of nitrogen through the ecosystem. The current status of this problem will be described in this section.

After N₂, nitrous oxide (N₂O) is the most abundant form of nitrogen in the troposphere. Its spatial distribution appears to be relatively uniform, but temporal fluctuations have been interpreted as implying an atmospheric residence time of from 4 to 70 years for this gas (refs. 10 and 66). Chemical destruction in the stratosphere alone would result in a longer lifetime of 118 to 160 years (ref. 67). With an atmospheric abundance of 0.25 to 0.30 ppm (1800 to 2160 Mt as N₂O), this range of lifetime implies source and sink strengths ranging from 11.3 Mt/yr to 540 Mt/yr. Although the source of atmospheric N₂O is clearly denitrifying bacteria, there is still a problem in identifying a sink of the appropriate magnitude. The role of the oceans in this regard is a subject of debate. Hahn (ref. 68) identified the oceans as a possible net source of N₂O, whereas McElroy et al. (ref. 69) believe that a flux of N₂O into the oceans may exist and provide the necessary sink. More data are required to assess accurately the role of the oceans in the nitrogen cycle.

Nitrous oxide is of importance because of its fundamental role in controlling the abundance of stratospheric ozone. In the stratosphere, N₂O dissociates by reaction with O(¹D) to form nitric oxide which catalytically reduces the

ambient ozone. N_2O also has an absorption band at $7.78\ \mu\text{m}$, and it has been estimated that a doubling of its concentration could result in a global mean increase in surface temperature of $0.68\ \text{K}$ (ref. 65). Because of the strength and position of the N_2O $7.78\text{-}\mu\text{m}$ band, it is the second most important absorber of thermal IR radiation (after CO_2 and neglecting the highly variable water vapor). The gas is of potential climatological significance due to both its thermal IR and chemical properties.

Ammonia (NH_3), the next most abundant form of atmospheric nitrogen, exhibits its strong spatial and temporal variabilities (ref. 70). There is a strong decrease of NH_3 with altitude, the concentration above $2\ \text{km}$ being about one-third of the ground-level value. Seasonally, mean ground-level NH_3 concentrations may vary from about $6\ \text{ppb}$ in summer to $2\ \text{ppb}$ in winter over land areas, but over the oceans there is a sharp decrease to about 0.2 to $1.0\ \text{ppb}$. The natural source of atmospheric NH_3 is bacterial decomposition of biologically fixed nitrogen found in plant tissues. The magnitude of this production depends on soil type, temperature, pH, and moisture content. Dawson (ref. 12) has recently calculated a soil source of $47\ \text{Mt/yr}$ of NH_3 from unperturbed land on a global basis. This source would be balanced by corresponding rainout and dry deposition. The atmospheric residence time of NH_3 is about a week before it is removed by precipitation.

An anthropogenic source of ammonia results from the volatilization of ammonium contained in nitrogenous fertilizers applied to agricultural soils. The remainder of the fertilizer nitrogen is assimilated by the biomass or undergoes transfer from the inorganic nitrogen soil to other reservoirs by processes noted subsequently. The quantitative relationship between these processes is not established, though it likely depends on the same soil variables described previously (ref. 12). Ammonia is thus strongly coupled with the processes affecting the cycling of nitrogen through the ecosystem via its interactions in the biosphere.

The oxides of nitrogen, NO and NO_2 , are the least abundant tropospheric nitrogen species. Their global distribution and background concentration are poorly known in the troposphere. Recent measurements by Noxon (ref. 11) indicate values of the order of $0.1\ \text{ppb}$ or less. Tropospheric sources for NO_x are combustion processes and lightning (10 to $40\ \text{Mt/yr}$ (refs. 71 and 72)) and denitrification of soil nitrogen. NO_x plays an important role in tropospheric chemistry involving the production and loss of ozone (ref. 33) and the effect of CO emissions on CH_4 abundances (ref. 64). Its global mean background concentration must be much better established.

The nitrogen cycle is schematically represented in figure 7. The reservoir values are similar to those stated in published reviews (refs. 24 and 73) but have been adjusted to be consistent with observed C/N ratios of $80/1$ for the living terrestrial biomass and $10/1$ for other biospheric reservoirs.

Perturbations to the Nitrogen Cycle

Man's intervention in the nitrogen cycle is largely through the production of nitrogen oxides in combustion and the manufacture and use of nitrogen fertil-

izers. As seen in figure 7, fertilizers add fixed nitrogen to the inorganic soil reservoir from which it begins cycling through the ecosystem. In 1959 the use of fertilizers was responsible for the fixation of 3.5 Mt/yr of N. This had grown to 40 Mt/yr by 1974 (ref. 74) and could reach 200 Mt/yr by 2000. Biological fixation rates are uncertain, particularly for the oceans. The fixation rate due to the land biomass has been put at 44 Mt/yr of N by Delwiche (ref. 73) and at 175 Mt/yr by Hardy and Havelka (ref. 75). The marine fixation rate has been estimated to be 10 Mt/yr of N (ref. 69). Thus, if the lower biological fixation rates are correct, man's contribution to nitrogen fixation is already equal to the natural source, or, if the higher biological fixation rates are accepted, it will become so by the year 2000. The consequences of this potentially large anthropogenic source of fixed nitrogen have been the subject of several papers (refs. 76 to 79).

Figure 7 indicates four major reservoirs which contain the nitrogen cycling through the ecosystem: atmosphere, land, ocean, and biosphere. The atmosphere contains 4×10^9 Mt of nitrogen mostly as N_2 , but there is a subreservoir (not shown explicitly in fig. 7) of fixed atmospheric nitrogen which contains about 1 Mt of N and consists primarily of NO_x and NH_3 . The flow of nitrogen into this atmospheric subreservoir from the atmosphere results from lightning discharges (10 to 40 Mt/yr (refs. 71 and 72)) and combustion (20.7 Mt/yr (ref. 74)). Interest in perturbations to the nitrogen cycle centers on the interactions of the biosphere with the other reservoirs and on the flow of nitrogen within the subreservoirs of the biosphere itself. The fixation flux, both natural and fertilizer, into the biosphere refers to processes of conversion of nitrogen from the biologically unutilizable N_2 to forms in which it can be used as nutrients, ammonium (NH_4^+), nitrate (NO_3^-), and nitrite (NO_2^-). The reverse process is denitrification which produces either N_2 or N_2O .

Within the land biosphere, three reservoirs are indicated: the living biomass, which contains about 7500 Mt of N; dead organic matter, called humus on land, which contains about 10^5 Mt of N; and the inorganic nitrogen pool, smallest of the three subreservoirs, containing about 5000 Mt of N. The flow of nitrogen into the biomass by natural fixation results from the activities of a multitude of microorganisms, either free-living or living in association with plants, that are able to utilize the energy stored in the products of photosynthesis to break the N_2 bond and fix nitrogen into forms which may be used for the synthesis of protein, amino acids, and other organic compounds. This process essentially represents a flow of nitrogen directly from the atmosphere to the biomass subreservoir. Fertilizer, by contrast, adds fixed nitrogen to the inorganic soil reservoir which consists of soluble nitrate and nitrite. From the inorganic nitrogen pool, the nitrogen may be assimilated by the biomass, which is the goal of fertilization; it may be immobilized, which means transferred to the organic nitrogen reservoir by bacterial assimilation or by sequestering of ammonia in clay particles; it may be lost by leaching from the soil, which may lead to problems such as the eutrophication of lakes; or it may be denitrified by denitrifying bacteria. The present debate on the impact of fertilizer nitrogen centers on the relative efficiencies and characteristic times for these loss processes.

The denitrification flux from the inorganic soil reservoir to the atmosphere is shown with a question mark in figure 7 since estimates published in

the literature vary substantially (e.g., 43 Mt/yr (ref. 73) and 210 Mt/yr (ref. 24)). Even if the flux is large, it is of possible importance only if a significant part of it consists of N_2O rather than N_2 . Significance, in this context, must be judged relative to the magnitude of other sources and sinks of atmospheric N_2O and these, as noted previously, are themselves a subject of debate. Finally, if these N_2O parameters were firmly established, there is still the uncertainty of the effect of a given N_2O increase on stratospheric ozone.

Johnston (ref. 67) has recently published a review of this subject in which he sought to place limits on the values of the variables described in the previous paragraph. The fraction of nitrogen fertilizer that is rapidly denitrified, β in Johnston's analysis, is highly uncertain. For a worst-case analysis of ozone reduction, β may be taken to be 1. The fraction of N_2O in denitrified gases α is taken to be in the range $0.025 < \alpha < 0.4$ by Johnston based on his review of the available data. As Johnston notes, these are estimates, not rigorous bounds. The importance of denitrified N_2O relative to other sources and sinks is discussed by Johnston in terms of the equivalent problem of the atmospheric residence time of N_2O . Large natural sources and sinks, which would minimize the impact of a given nitrous oxide flux in denitrified gases, correspond to shorter values of the residence time τ . From consideration of observed temporal and spatial variabilities of N_2O on the one hand (implying a short residence time and giving a lower bound to τ (ref. 66)) and the rate of stratospheric destruction on the other (giving the upper bound), the range of N_2O residence time given by Johnston is 5 years $< \tau < 160$ years. Johnston seeks to place limits on the combinations of α and τ consistent with identified nitrogen fixation sources, and he concludes that for reasonable values of these variables, the maximum ozone reduction due to added 100 Mt/yr of N from fertilizer will lie between 0.4 and 12 percent and will occur within a few decades for 1- to 2-percent reduction or over hundreds of years for larger (≈ 10 -percent) reductions.

This analysis is based on estimates of the uncertainties involved in the parameters of the biospheric portion of the nitrogen cycle and does not discuss the possible impact of the uncertainties in the many chemical rate constants involved in the stratospheric modeling of ozone reductions (refs. 80 and 81), as Johnston clearly states. However, as noted in the discussion of tropospheric ozone, the revision of a single chemical rate constant involved in a complex system can substantially alter the model conclusions. It is not possible to be even order-of-magnitude quantitative regarding the impact of nitrogenous fertilizers on stratospheric ozone and even Johnston's wide limits may be overly restrictive.

The nitrogen and carbon cycles are strongly coupled through the biosphere, but potential consequences of this fact have yet to be quantitatively explored. One aspect of this coupling was noted previously in describing the constancy of the ocean biomass in the face of increased CO_2 input to the oceans. This presumed constancy results from the fact that nitrogen, rather than carbon, is a limiting nutrient in the oceans. For example, the 5000 Mt/yr of carbon currently entering the atmosphere because of fossil fuel burning (fig. 2) could be assimilated entirely by the ocean biomass if an increased nitrogen input of 400 Mt/yr to the oceans occurred, assuming a C/N ratio of 12 for the ocean bio-

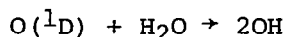
mass. This nitrogen input is 10 times the 1974 nitrogen fertilizer use and twice the projected use for the year 2000 (ref. 74). The assimilation of this amount of nitrogen and carbon would require a yearly increase of 4 percent in the ocean biomass. There are yet insufficient data to determine the actual runoff of nitrate into the oceans, but the data discussed by Commoner (ref. 82) on nitrates in U.S. river systems show that this runoff has increased by a factor of 3 to 5 in the past 20 years.

Phosphorous, another limiting nutrient for the ocean biomass, is also being discharged into the oceans from land areas. The SCEP report (ref. 83) gives the 1968 U.S. mean phosphorous content of runoff as 0.44 Mt.

In view of the increasing anthropogenic supply of limiting nutrients to the ocean biomass, it is conceivable that the increase in atmospheric CO₂ could be moderated in future years, but the amounts of these nutrients required to reverse the effect are relatively large compared with projected usage. This problem deserves quantitative study with attention to the role of phosphorous as a limiting oceanic nutrient and to the fraction of fertilizer nitrogen which finds its way to the oceans.

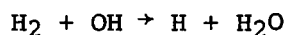
HYDROGEN GROUP

The most abundant member of this group is water vapor (H₂O) which is present in the atmosphere as a consequence of evaporation of liquid water at the Earth's surface. Water vapor is chiefly responsible for the greenhouse effect through its strong absorption of infrared radiation, and it is an essential precursor for the OH radical produced through the reaction



The amount of H₂O in the atmosphere is highly variable and little influenced by human activities, and its properties, therefore, will not be described in further detail.

Molecular hydrogen (H₂) is the next most abundant member of this group, having a concentration of about 0.5 ppm. The prevailing view (ref. 13) is that H₂ is formed mainly by bacterial fermentation in soils and from the photodissociation of formaldehyde, one of the intermediate products in the photooxidation of methane, but the relative importance of these two paths is uncertain. The sink for H₂ is reaction with OH:



The most important member of this group in influencing the concentrations of many trace tropospheric species is the hydroxyl radical (OH). Reaction with OH is the dominant removal mechanism for constituents which are shielded from dissociation and are not removed via interaction with the hydrologic cycle. This is the case for many of the gases released into the atmosphere as a result of human activities, such as CO, NO₂, various halogenated methane compounds (CHCl₂F, CHClF₂, CHCl₃, CH₃Cl), halogenated ethylenes, and CH₃CCl₃. In many cases, reaction of the halogenated hydrocarbons with tropospheric OH removes a

large potential source of stratospheric chlorine and thus reduces a potential harmful impact on the ozone layer. Recent measurements (refs. 14, 15, and 47) show tropospheric mean OH concentrations of the order of 10^6 cm^{-3} . Reaction with OH is also the dominant removal mechanism for reduced gases of biological origin such as CH_4 and H_2S .

Hydroperoxyl radicals (HO_2) are formed mainly by the reaction of CO and H_2 with OH. Because anthropogenic emissions of CO are now considered to represent a large fraction of the total atmospheric CO source, the potential exists for man's intervention in determining the background abundances of OH and HO_2 radicals in the troposphere. HO_2 radicals are not as reactive toward many species as are OH radicals, and a shift in the odd hydrogen balance ($\text{OH} + \text{HO}_2$) could have consequences in determining the abundances of compounds mainly lost by reaction with OH, as was pointed out recently by Sze (ref. 40), Chameides et al. (ref. 41), and Hameed et al. (ref. 64).

SULFUR GROUP

The abundances, sources and sinks, and photochemistry of atmospheric sulfur compounds are all poorly understood relative to oxygen, carbon, or nitrogen compounds. Various sulfur species are important components of air pollution in many parts of the world. The anthropogenic input to the sulfur cycle is clearly significant and likely to increase in magnitude, but the consequences of these facts have been relatively little explored. The details of the sulfur cycle have been reviewed by Friend (ref. 16), Kellogg et al. (ref. 84), Robinson and Robbins (ref. 35), and Junge (ref. 25).

The importance of sulfur as a pollutant derives mainly from the properties of sulfur dioxide (SO_2). This gas is toxic to plants and animals and is oxidized in the atmosphere to sulfuric acid (H_2SO_4). It thus acts as an aerosol precursor, may have an effect on cloud formation, and is therefore of potential climatological significance. The H_2SO_4 may lower the pH of rainwater with deleterious consequences. Toxicity of SO_2 and acid rain are likely to be confined to local- and regional-scale effects because of the short (≈ 1 week) residence time of atmospheric sulfur, but changes in aerosol or cloud properties are global-scale phenomena.

The chemistry of the atmospheric portion of the sulfur cycle over land is shown in figure 8. Volcanic activity is a modest source of natural SO_2 (2 Mt/yr of S) compared with industrial output (65 Mt/yr of S). The largest natural source of atmospheric sulfur is decay of organic material in the biosphere (58 Mt/yr of S over land). This input is in the form of reduced sulfur such as hydrogen sulfide (H_2S) and organic sulfides (dimethyl sulfide (DMS), dimethyl disulfide (DMDS)) and is rapidly oxidized to SO_2 by reactions with atmospheric trace constituents (ref. 85). The oxidation mechanism is as yet unclear. The lifetime of reduced sulfur in the atmosphere is of the order of hours, but reaction of H_2S with O_3 results in a lifetime of a month or more. Reaction of H_2S with OH is faster but still results in a lifetime of a few days. It may be that oxidation of reduced sulfur in the atmosphere results from reaction of organic sulfides with NO_x , but this mechanism is uncertain.

Sulfur dioxide is itself oxidized in the atmosphere with a lifetime of hours. This may occur by gas-phase reaction with OH and HO₂ radicals to form SO₃ which is then rapidly absorbed in water vapor to form sulfuric acid, or the SO₂ may undergo heterogeneous removal by reaction with dissolved O₂ in water droplets. The relative importance of these mechanisms is uncertain, but it is difficult to account for the short SO₂ lifetime solely by gas-phase chemistry.

A schematic diagram of the sulfur cycle is shown in figure 9. The magnitudes of the sulfur reservoirs and fluxes are based on the model of Friend (ref. 16) but have been adjusted where necessary to maintain the observed N/S ratio of 7 (ref. 86). The large impact which human activity has on the sulfur budget is obvious. The 65 Mt/yr of sulfur emitted to the atmosphere has a substantial influence on pollution on the urban and regional scale, but whether there are global effects associated with this input or with potentially larger SO₂ inputs is a largely unexplored problem. The 26 Mt/yr of sulfur added to the soil in fertilizers is a significant and growing fraction of the total soil input of 147 Mt/yr. Possible ecological consequences of this addition have not been addressed.

HALOGEN GROUP

The concentration of halogen compounds in the atmosphere is much less than that of the other groups thus far discussed, being generally of the order of parts per billion or less. Recent research interest in this group derives from the fact that the anthropogenic contribution to atmospheric halogens is a clearly significant source and that these species are believed to efficiently reduce stratospheric ozone and in some cases to possess radiative properties of possible climatic significance (ref. 87).

The most abundant, naturally occurring halogens are the marine organic halogens, methyl chloride (CH₃Cl), methyl bromide (CH₃Br), and methyl iodide (CH₃I) (ref. 18) which are present in abundances of about 780 ppt, 10 ppt, and 1.2 ppt, respectively.

Anthropogenic contributions to the halogen budget consist primarily of the chlorofluoromethanes (CCl₃F and CCl₂F₂) and carbon tetrachloride (CCl₄) (ref. 88). In the early 1970's, the tropospheric concentrations of CCl₃F, CCl₂F₂, and CCl₄ were about 90 ppt, 100 ppt, and 120 ppt, respectively (ref. 89).

Most of the concern over atmospheric halogens centers on the ability of the long-lived industrial compounds CCl₃F and CCl₂F₂ to diffuse into the stratosphere where they will dissociate and release chlorine, leading to a postulated reduction of ozone. A review of the extensive literature on this subject is not within the scope of this paper. (See refs. 17 and 90.)

The accumulation of chlorofluorocarbons and CCl₄ in the troposphere could have climatic consequences; however, Ramanathan (ref. 87) states that a surface-temperature increase of 0.8 K could occur if the concentrations of CCl₃F and CCl₂F₂ were each increased to 2 ppb, about a twentyfold increase over present levels. Wang et al. (ref. 65) derive a maximum surface-temperature increase of

0.54 K for the same assumed increase in CCl_3F and CCl_2F_2 concentrations. The difference in these two results is to some extent due to the fact that Wang et al. use more recently measured band intensities for the ν_1 (9.13 μm) and ν_8 (10.93 μm) bands of CCl_2F_2 and the ν_1 (9.22 μm) and ν_4 (11.82 μm) bands of CCl_3F . These recent measurements are roughly half the older values used by Ramanathan.

CONCLUDING REMARKS

Man's intervention in the geochemical cycles which control the composition of the atmosphere has only recently been appreciated. Attempts to predict the consequences of such interventions now occupy the efforts of a growing number of researchers in many fields. These efforts are necessarily of a broadly interdisciplinary character involving biologists, chemists, geologists, oceanographers, meteorologists, aeronomers, and others seeking answers to the many questions of environmental concern which have been raised by man's activities.

Interest in the oxygen group, from the point of view of its influence on pollution and climate, centers on the role of ozone and atomic oxygen in tropospheric photochemistry. Ozone is the precursor of all global-scale tropospheric photochemistry, and understanding of the processes which produce and destroy ozone in the troposphere is thus of fundamental importance to the understanding of the atmospheric phase of other geochemical cycles. This problem is currently an active area of research, but the major questions regarding the relative importance of transport and photochemistry in establishing the ozone distribution remain unanswered.

Man's intervention in the carbon cycle results chiefly from the burning of fossil fuels and is mainly manifested in the increasing atmospheric concentration of carbon dioxide (CO_2). The general problem is to predict future atmospheric levels of CO_2 and the climatic consequences of such levels. The major issues involved in predicting these levels presently include the role of deforestation as a CO_2 source and the present and future effectiveness of the oceans as a CO_2 sink. The major difficulties in predicting the climatic consequences of increased CO_2 abundances are with properly including climate feedback mechanisms, such as albedo and cloud cover changes, and ocean coupling in mathematical models.

A perturbation to the nitrogen cycle is occurring as a result of the increasing use of fertilizers in agriculture. The annual industrially fixed nitrogen resulting from this use is either already or by the end of the century will be equal to the amount of nitrogen fixed naturally. It has been suggested that one consequence of this intervention in the nitrogen cycle will be an increase in the abundance of nitrous oxide (N_2O) as the denitrification rate adjusts to the increased fixation rate. Additional N_2O could result in a decrease in the amount of stratospheric ozone and might also make a contribution to the greenhouse effect. Uncertainties abound in this problem. Among those that have been discussed in the literature are the atmospheric residence time of N_2O (5 to 160 years), the fraction of denitrified fertilizer nitrogen that enters the atmosphere as N_2O (0.025 to 0.4), the fraction of fertilizer nitrogen that is rapidly denitrified (highly uncertain), and the effect of a

given N_2O increase on stratospheric ozone and the greenhouse effect (perhaps a factor-of-2 uncertainty).

The hydrogen group is chemically active in the atmosphere and is thus subject to perturbations. Changes in the abundances of the components of this group would not (excepting water vapor) have a direct influence on pollution or climate. The extremely active hydroxyl radical, however, reacts strongly with every other major atmospheric group, and changes in its mean abundance could have far-reaching consequences.

Man is also intervening in the sulfur cycle, but global-scale consequences of this influence have yet to be identified. Most of the sulfur dioxide that enters the atmosphere is of industrial origin and can potentially alter such things as the atmospheric aerosol loading and the acidity of rainfall over at least mesoscale regions. The 26 Mt/yr of sulfur added to the soil in fertilizers is relatively large compared with natural sources. If substantially increased coal burning occurs in the future in response to shortages of alternate fuels, the magnitude of the industrial sulfur source will increase still further. It is essential that some attempts to understand the potential impact of this fact be made in future research.

The halogens are relatively inactive chemically in the troposphere, and recent research interest has centered on the reduction of stratospheric ozone which might be a consequence of their release into the atmosphere. Some of the components of this group do, however, have absorption bands in the thermal IR region, and it has been suggested that their continued buildup in the troposphere might contribute more than 0.5 K to the greenhouse effect.

It must be borne in mind that the elemental cycles of oxygen, carbon, nitrogen, hydrogen, and sulfur which have been discussed individually are strongly coupled with one another through the biosphere and atmosphere. The carbon and oxygen cycles are coupled over time scales up to $\sim 10^3$ years by the biological processes of photosynthesis, respiration, and decay and over longer time scales by geochemical interactions. The carbon, nitrogen, and sulfur cycles are coupled by the nutrient needs of the biosphere and to a lesser extent by chemical interactions in the atmosphere. The increasing abundance of carbon dioxide resulting from human intervention in the carbon cycle may not in itself permit an expansion of the biomass since other nutrients such as nitrogen and phosphorous are the limiting factors. On a small ecological scale, the eutrophication of lakes and streams provides examples of the extent to which natural cycles may be perturbed when limiting nutrients are supplied by man. With the possible exception of the interactions of the carbon-oxygen cycle, the interactions between the elemental cycles have not yet been explored in adequate quantitative detail. It is likely that as understanding increases, interrelationships among the various geochemical cycles will emerge and that the interdisciplinary nature of this research will be enhanced.

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TABLE I.- TROPOSPHERIC COMPOSITION

Species	Chemical symbol	Fractional abundance	Lifetime	Thermal IR band, μm	Sources (a)	Sinks (a)	References
Oxygen group:							
Oxygen (molecular)	O_2	$b_{0.2}$	10^6 yr		B	B, P	4
	$\text{O}_2(^1\Delta_g)$	10^{-13}	0.26 s		C	C	
Oxygen (atomic)	O	10^{-16}	10^{-5} s				
	$\text{O}(^1D)$	10^{-23}	10^{-9} s		C	C	
Ozone	O_3	$b_3 \times 10^{-8}$	2 mo	9.6	P, C	P, C	5
Carbon group:							
Methane	CH_4	$b_{1.4} \times 10^{-6}$	4 yr	7.7	B	C	6
Non-methane hydrocarbons		$\sim 10^{-9}$					7
Methyl radical	CH_3	10^{-21}	10^{-10} s		C	C	
Methoxy radical	CH_3O	10^{-15}	0.1 s		C	C	
Methylperoxy radical	CH_3O_2	10^{-11}	10^3 s		C	C	
Methylhydroperoxy radical	CH_3OOH	10^{-11}	2 d		C	P, C	
Formyl radical	HCO	10^{-22}	10^{-8} s		C	C	
Formaldehyde	H_2CO	$b_4 \times 10^{-10}$	0.4 d		C, A	C	4
Acetaldehyde	CH_3CHO				C	C	
Carbon monoxide	CO	$b_{1.2} \times 10^{-7}$	4 mo		C, A	C, P	8
Carbon dioxide	CO_2	$b_{3.3} \times 10^{-4}$	5 yr	15	B, A	B, P	9
Nitrogen group:							
Nitrogen	N_2	$b_{0.8}$	10^6 yr		B, P	B, P	4
Nitrous oxide	N_2O	$b_{3.3} \times 10^{-7}$	20 yr?	7.8, 17	B, P	C	10
Nitric oxide	NO	10^{-11}			A, B	C	
Nitrogen dioxide	NO_2	$b_{10^{-10}}$		7.6	A, B, C	C	11
Nitrogen trioxide	NO_3	10^{-14}	15 s		C	C	
Dinitrogen pentoxide	N_2O_5	10^{-14}	15 s		C	C	

^aKey to entries in sixth and seventh columns: A - anthropogenic, B - biological or microbiological, C - chemical, and P - physical.

^bMeasured value. Other entries in third column were calculated.

TABLE I.- Continued

Species	Chemical symbol	Fractional abundance	Lifetime	Thermal IR band, μm	Sources (a)	Sinks (a)	References
Nitrous acid	HNO ₂	10 ⁻¹²	10 ³ s	5.9, 7.5, 11.3, 21.8 10.53	C	C	12
Nitric acid	HNO ₃	10 ⁻⁹	1 week		C	P, C	
Ammonia	NH ₃	10 ⁻⁹	1 week		B, A	C, P	
Amino radical	NH ₂	10 ⁻²¹	10 ⁻⁵ s		C	C	
Aminoxy radical	NH ₂ O	10 ⁻¹⁶	1 s		C	C	
Aminoperoxy radical	NH ₂ O ₂	10 ⁻¹²	1 min		C	C	
Nitroxyl radical	HNO	10 ⁻¹⁴	10 s		C	C	
Ammonium nitrate	NH ₄ NO ₃	10 ⁻¹⁰	1 week		C	P	
Hydrogen group:							
Hydrogen (molecular)	H ₂	5 × 10 ⁻⁷	10 yr	6.25, 10.0, 20.0	C, B, A	C	13
Hydrogen (atomic)	H	10 ⁻²¹	10 ⁻⁷ s		C	C	
Water	H ₂ O	0.014	1 week		P	P	4
Hydroxyl radical	OH	10 ⁻¹⁴	1 s		C	C	14, 15
Hydroperoxyl radical	HO ₂	10 ⁻¹¹	4 min		C	C	
Hydrogen peroxide	H ₂ O ₂	10 ⁻⁹	2 d		C	C	
Sulfur group:							
Hydrogen sulfide	H ₂ S	2 × 10 ⁻¹⁰	3 d	8.7, 7.3	B, A	C	16
Dimethyl sulfide	(CH ₃) ₂ S				B	C	
Dimethyl disulfide	(CH ₃) ₂ S ₂				B	C	
Sulfur dioxide	SO ₂	2 × 10 ⁻¹⁰	hours		B, A	C, P	16
Carbonyl sulfide	COS	5 × 10 ⁻¹⁰			B	C	
Thiyl radicals	HS	10 ⁻²¹	10 ⁻⁶ s		C	C	
Sulfoxy	SO	10 ⁻¹⁸	10 ⁻³ s		C	C	
Sulfur trioxide	SO ₃	10 ⁻²²	10 ⁻⁶ s		C	C	
Sulfurous acid	H ₂ SO ₃	10 ⁻¹⁰	1 week		C	P	
Sulfuric acid	H ₂ SO ₄	10 ⁻¹⁰	1 week		C	P	

^aKey to entries in sixth and seventh columns: A - anthropogenic, B - biological or micro-biological, C - chemical, and P - physical.

^bMeasured value. Other entries in third column were calculated.

TABLE I.- Concluded

Species	Chemical symbol	Fractional abundance	Lifetime	Thermal IR band, μm	Sources (a)	Sinks (a)	References
Halogen group:							
Trichlorofluoromethane (Freon 11)	CCl_3F	$b_{10^{-10}}$	50 yr	9.22, 11.82	A	C	17
Dichlorodifluoromethane (Freon 12)	CCl_2F_2	$b_2 \times 10^{-10}$	100 yr		A	C	17
Dichlorofluoromethane (Freon 21)	CHCl_2F	$b_{1.4} \times 10^{-11}$	2 yr		A	C	18
Chlorodifluoromethane (Freon 22)	CHF_2Cl		16 yr		A	C	
Carbon tetrachloride	CCl_4	$b_{10^{-10}}$	60 yr	12.99	A, B	C	17
Methyl bromide	CH_3Br	$b_{4.7} \times 10^{-12}$	1.5 yr	16.4, 10.5, 7.66, 6.92	A, B	C	18
Methyl chloride	CH_3Cl	$b_7 \times 10^{-10}$	1.4 yr	13.66, 9.85, 7.14	A, B	C	17
Methyl iodide	CH_3I	$b_{10^{-11}}$		18.76, 11.36, 7.99, 6.94	A, B	C	
Hydrogen chloride	HCl	10^{-9}	1 week		A, P	C	19
Chloroform	CHCl_3	$b_{9.4} \times 10^{-12}$	7 mo		A, B	C	18
Trichloroethylene	C_2HCl_3	$b_{8.2} \times 10^{-11}$	6 d		A	C	18
Tetrachloroethylene	C_2Cl_4	$b_{3.1} \times 10^{-11}$	5 mo		A	C	18
1,1,1 trichloroethane (methyl chloroform)	CH_3Cl_3	$b_7 \times 10^{-11}$	2.3 yr		A, B	C	18
Vinyl chloride	$\text{C}_2\text{H}_3\text{Cl}$		2 mo		A	C	
Phosgene	COCl_2	$b_2 \times 10^{-11}$			A	C	18
Noble gases:							
Argon	A	$b_{9.3} \times 10^{-3}$			P		20
Neon	Ne	$b_{1.8} \times 10^{-5}$			P		20
Krypton	Kr	$b_{1.1} \times 10^{-6}$			P		20
Xenon	Xe	$b_{9.0} \times 10^{-8}$			P		20
Helium	He	$b_{5.2} \times 10^{-6}$			P	P	20
Radon	Rn		3 d		P	P	

^aKey to entries in sixth and seventh columns: A - anthropogenic, B - biological or micro-biological, C - chemical, and P - physical.

^bMeasured value. Other entries in third column were calculated.

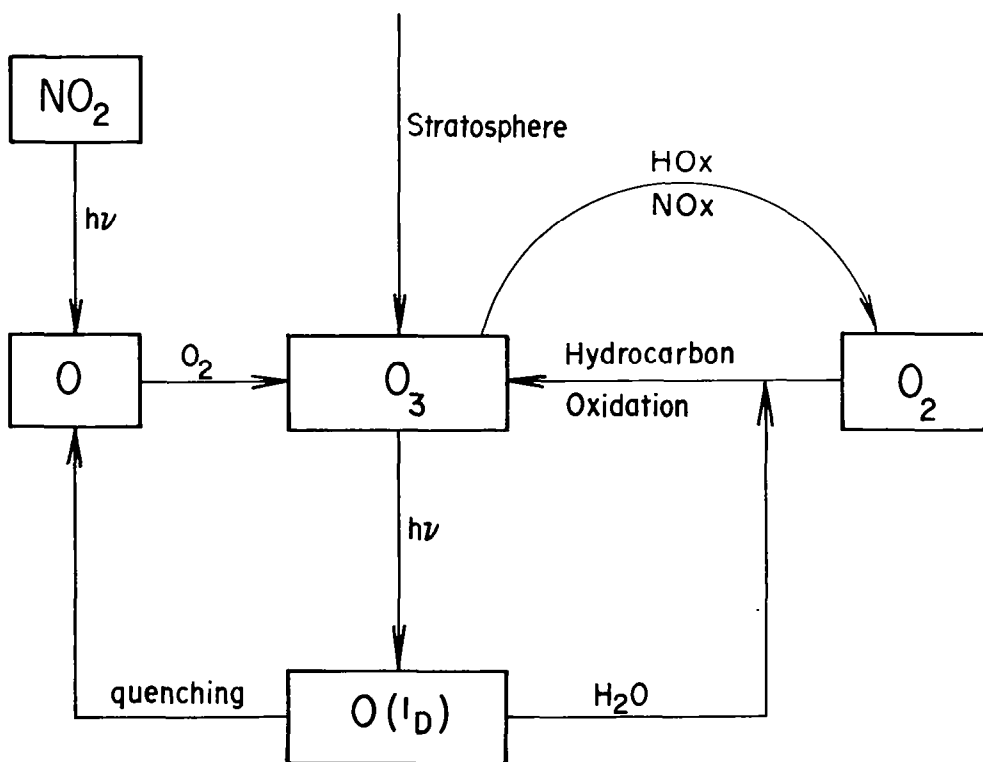


Figure 1.- Oxygen budget of troposphere.

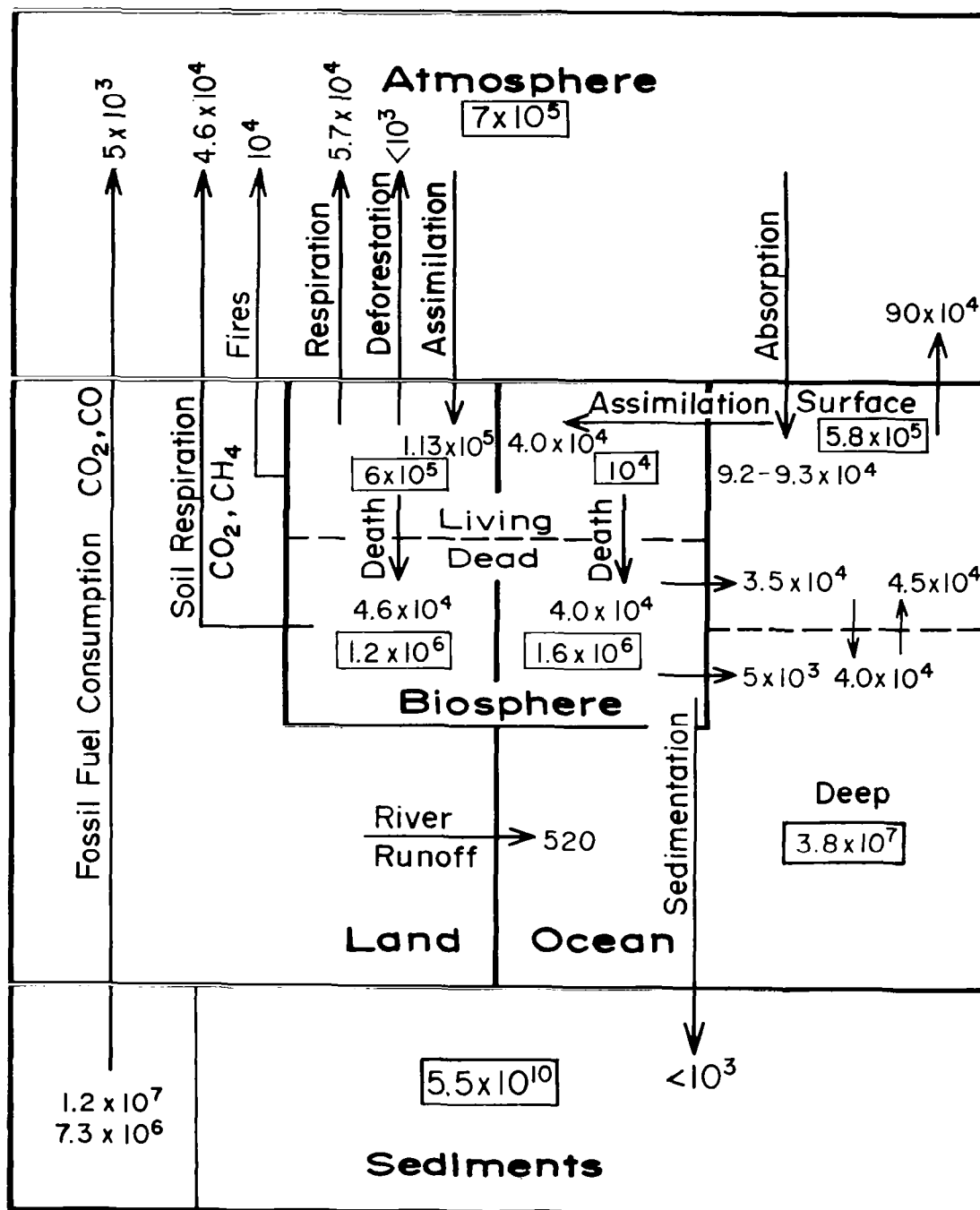


Figure 2.- Carbon cycle. The number of megatons of carbon (C) in indicated reservoirs is shown in boxes. Total fossil fuel carbon (1.2×10^7 Mt) and amount available for use (7.3×10^6 Mt) are shown at left of sediment reservoir. Fluxes between reservoirs are shown by arrows and given in Mt/yr of C.

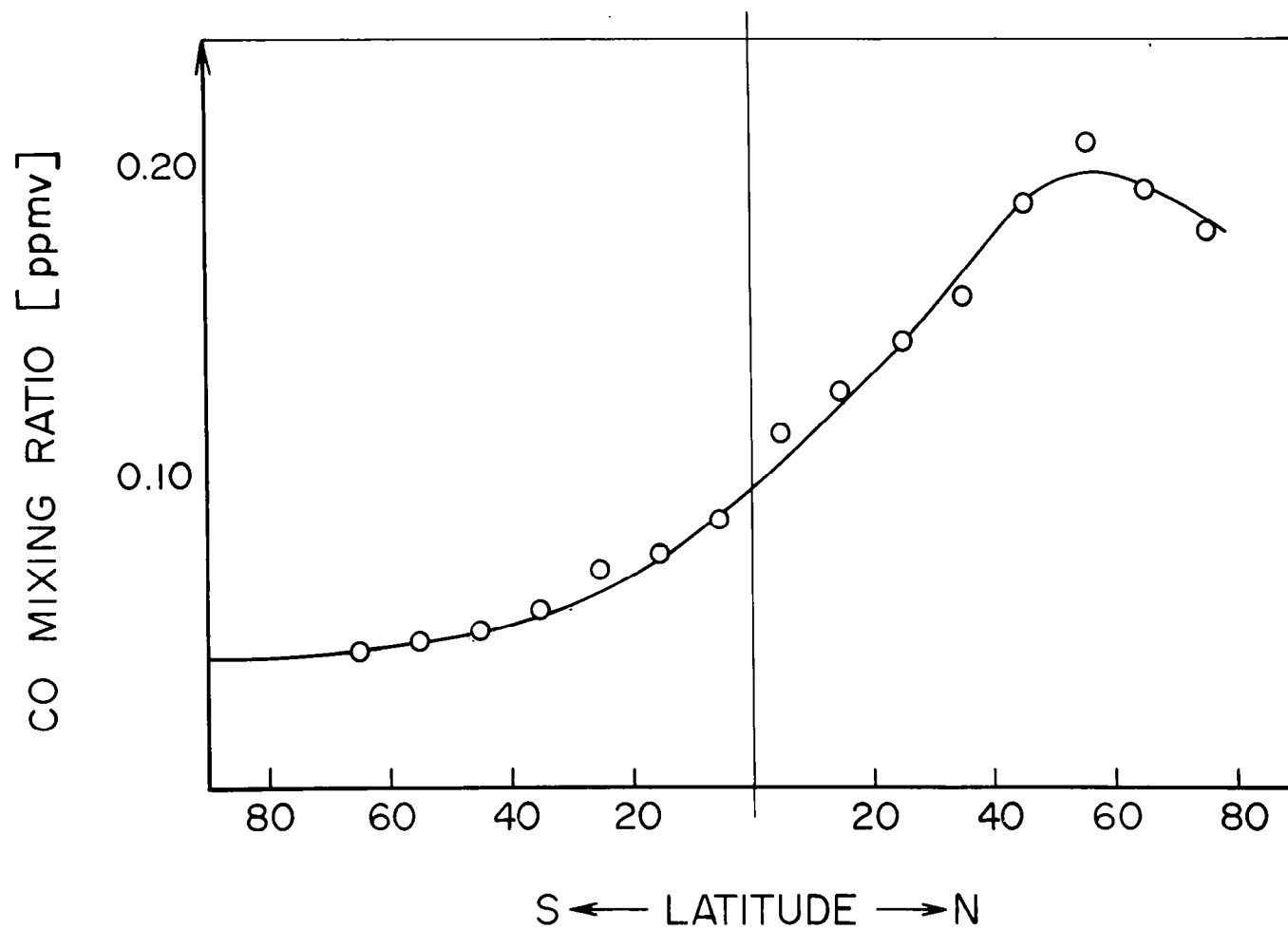


Figure 3.- Latitudinal variation of CO in troposphere. (From Seiler (ref. 8) with permission of publisher.)

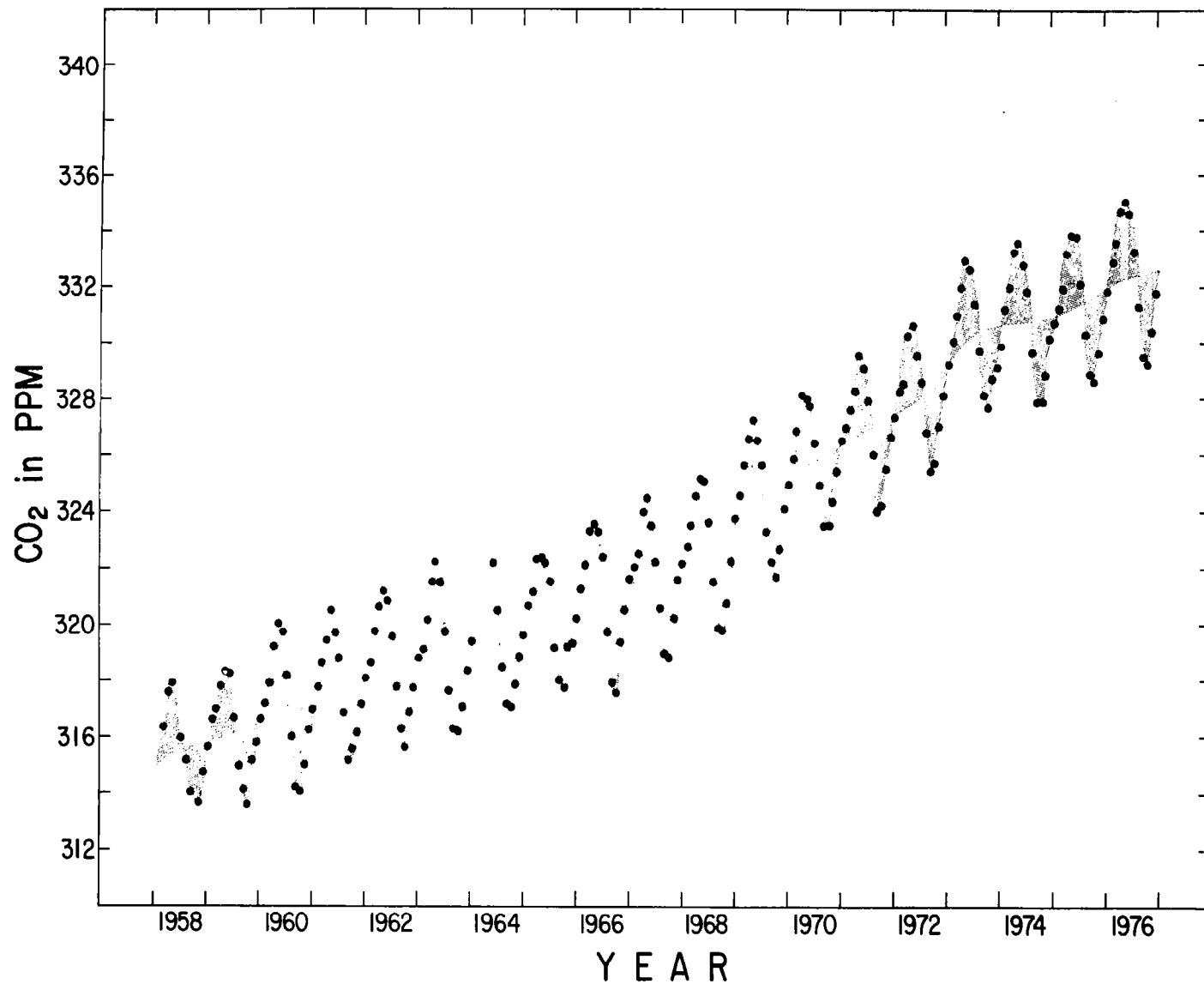


Figure 4.- Monthly average concentration of CO₂ in atmosphere at Mauna Loa Observatory, Hawaii, since beginning of monitoring in 1958. Seasonally adjusted long-term rising trend is indicated approximately by wavy line defined by shaded triangles. (Furnished by C. D. Keeling.)

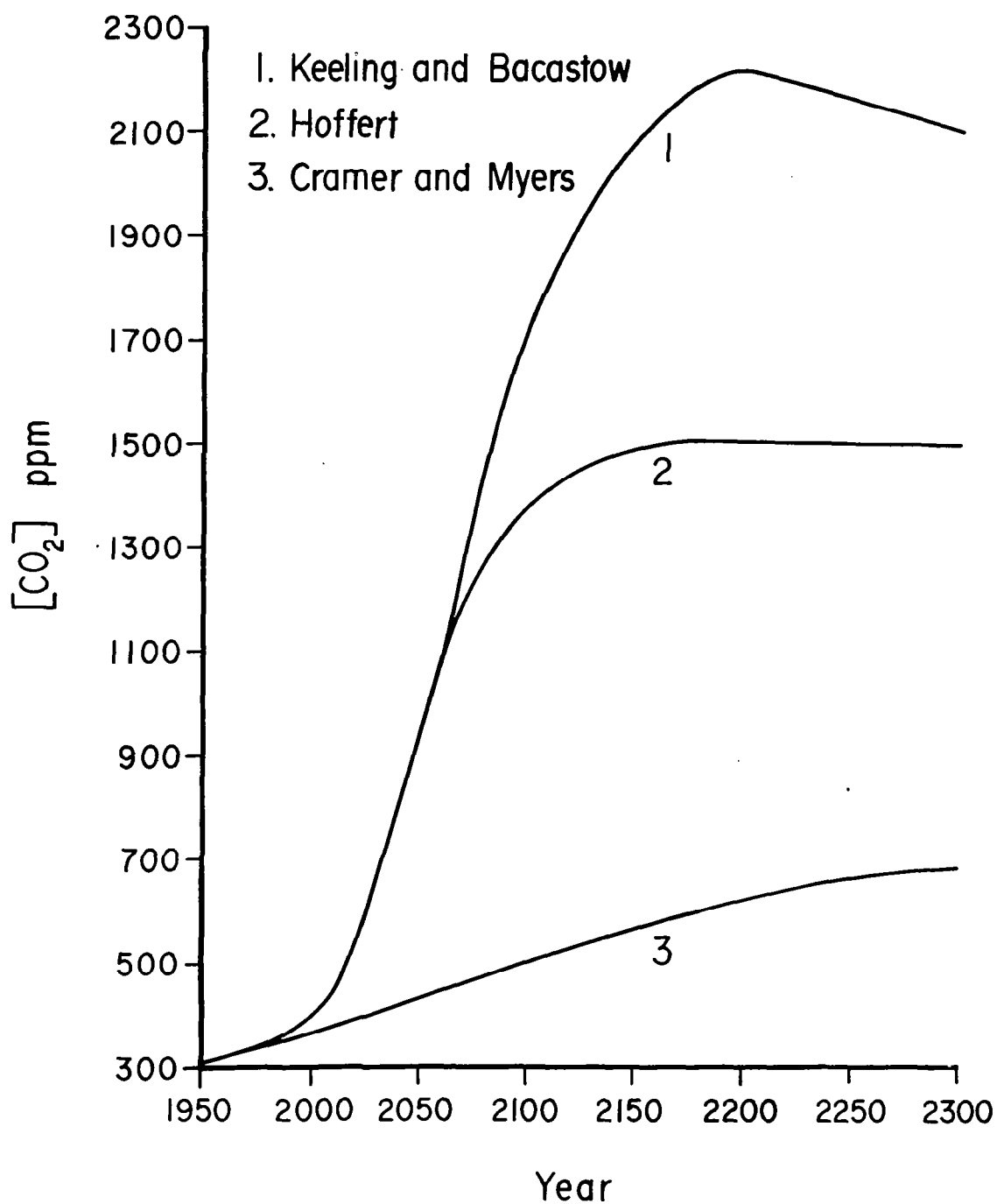


Figure 5.- Projected atmospheric CO₂ increases due to fossil fuel burning from three model studies.

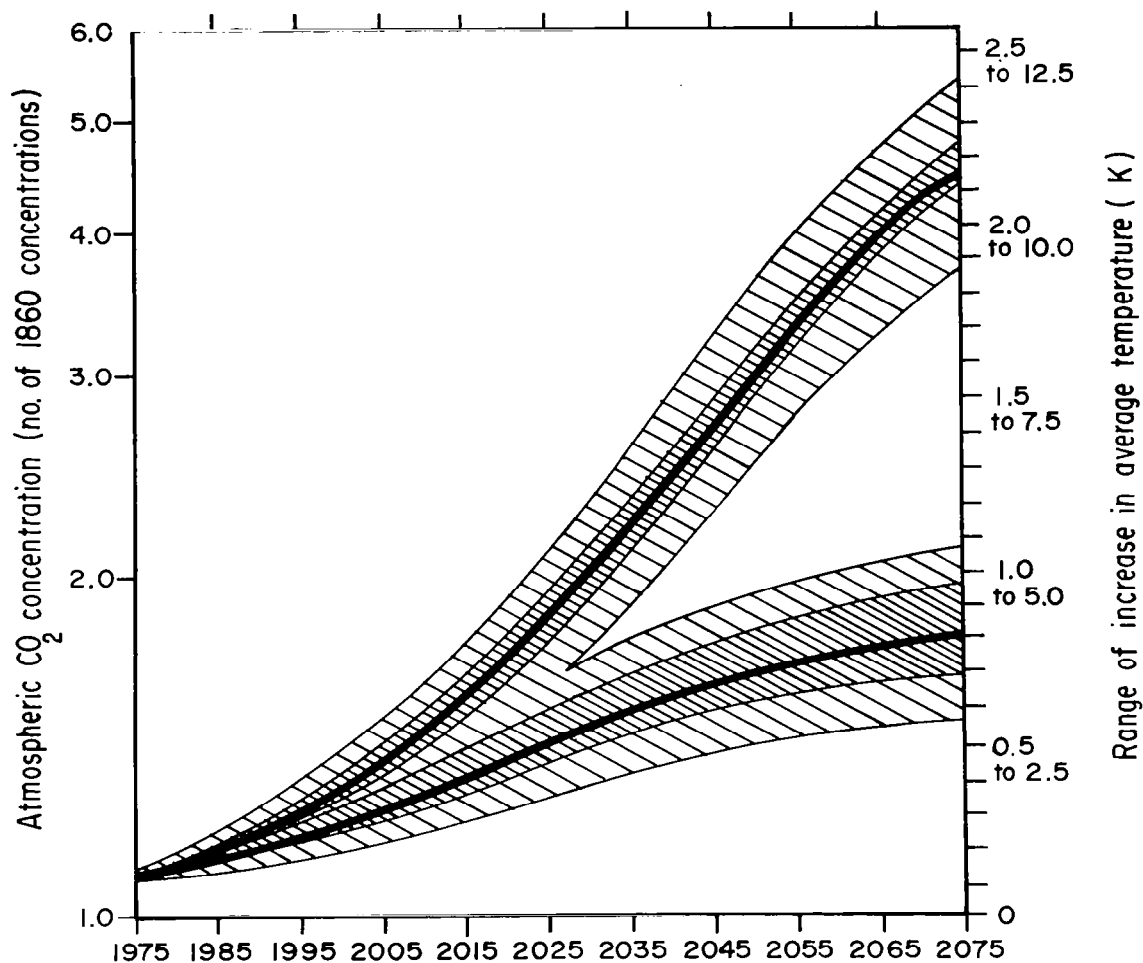


Figure 6.- Projected growth in atmospheric CO_2 and associated range of ΔT_s values for two scenarios of fossil fuel utilization. These curves show sensitivity of model to high and low use production scenarios (inner solid lines), assimilation of CO_2 by land biota (inner band), and oceanic uptake (outer band). The right vertical axis shows the range of uncertainty in ΔT_s for each value of CO_2 increase. (From Baes et al. (ref. 46) with permission of publisher.)

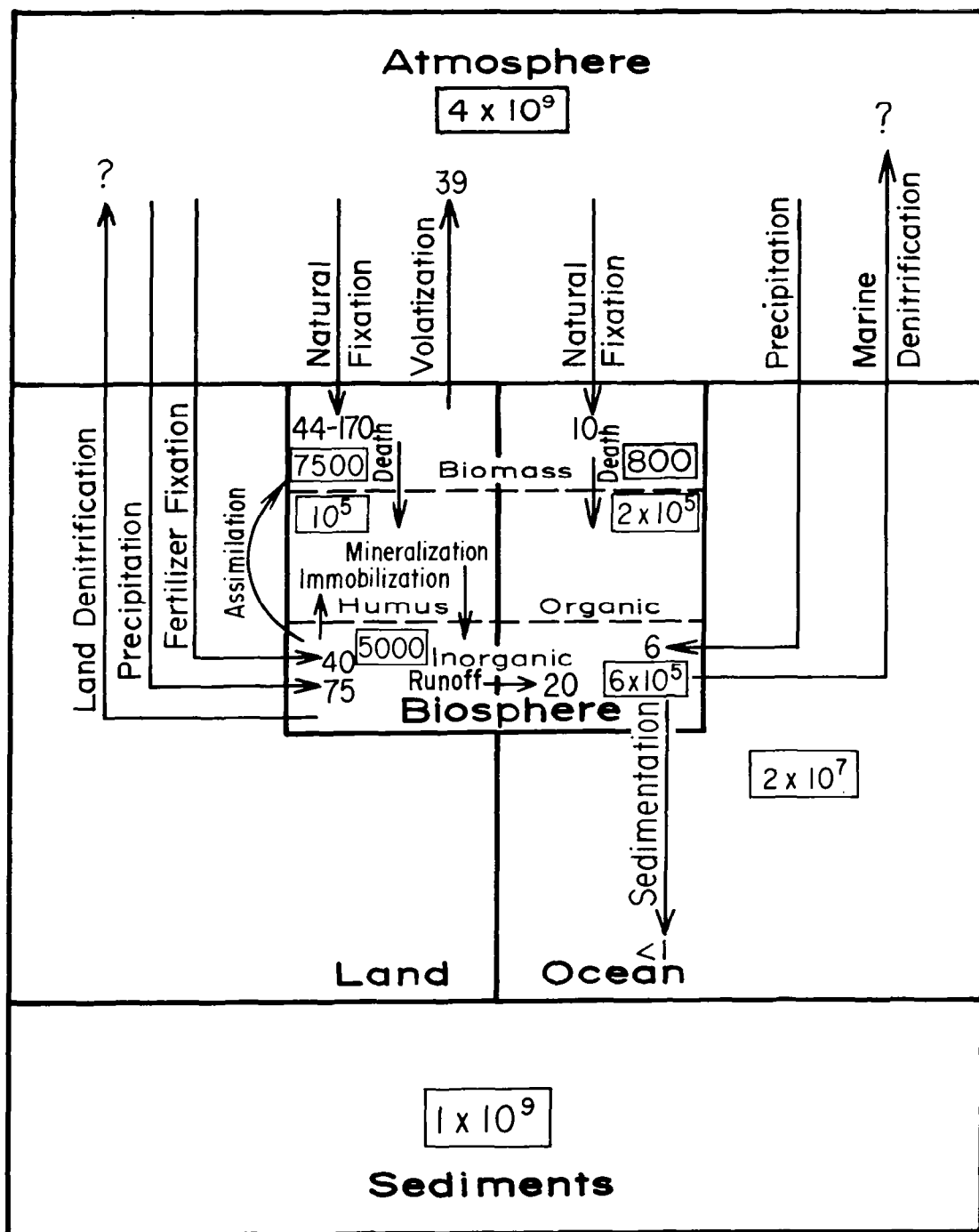


Figure 7.- Nitrogen cycle. The number of megatons of nitrogen (N) in indicated reservoirs is shown in boxes. Fluxes between reservoirs are shown by arrows and given in Mt/yr of N.

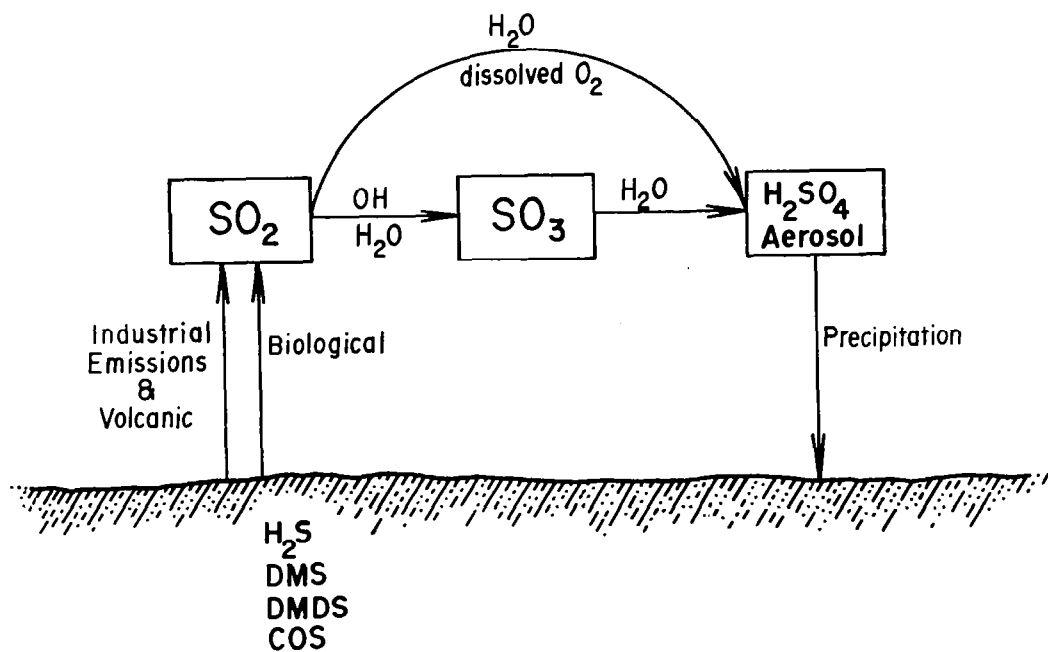


Figure 8.- Tropospheric sulfur chemistry over land. Biological sources emit reduced sulfides H_2S , DMS (dimethylsulfide), DMDS (dimethyldisulfide), and COS (carbonyl sulfide). Industrial and volcanic sources emit SO_2 directly.

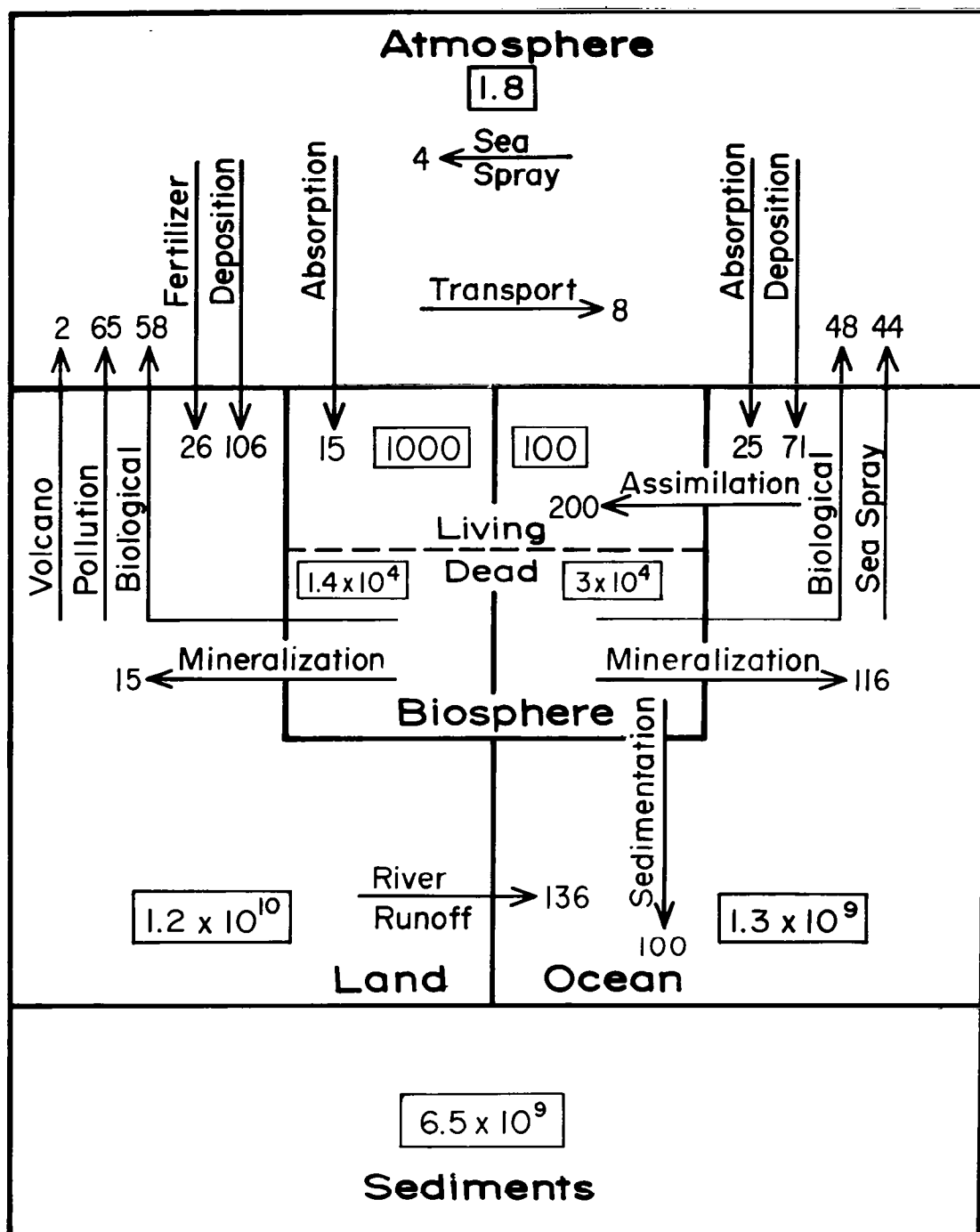


Figure 9.- Sulfur cycle. The number of megatons of sulfur (S) in indicated reservoirs is shown in boxes. Fluxes between reservoirs are shown by arrows and given in Mt/yr of S.